Corrosion stratifications on glass jewellery excavated beneath the market square in Kraków, Poland

Dominika Zabiegaj[1], Barbara Szala[2], Elżbieta Greiner-Wronowa[3]

[1] CNR, Institute for Energetics and Interphases; Genova, Italy
[2] AGH University of Science and Technology, Faculty of Geology, Geophysics and Environmental Protection;
al. Mickiewicza 30, 30-059 Krakow, Poland; e-mail: basia.szala@gmail.com
[3] AGH University of Science and Technology, Faculty of Materials Science and Ceramics;
al. Mickiewicza 30, 30-059 Krakow, Poland, e-mail: egrwrona@agh.edu.pl

Abstract: Glass has been one of the materials selected for its decorative purposes since early mankind. Its production was complex and varied all around the world, considering the sources of local materials used for its production as well technological knowledge about the manufacturing process. The aim of this work is to put some light on glass jewelry unearthed during the archeological excavations at the Main Market Square in Kraków, and to increase the importance of a stratifications investigation of ancient subjects by induced corrosion, using glass sensors.
The collected data helps to determinate the definitive condition of a historical object. This data will also help to establish the chemical nature of the corrosion products and the altered glass and metal surfaces. Moreover, the ring presented in this work can be considered to be from a small group of fine medieval jewelry corresponding to the upper class of the population, such as the nobility or wealthy merchants. Such individuals dealt with the exchange of goods with foreign countries. Because of a very limited amount of analytical material, only nondestructive analysis: scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDXS), X-ray diffraction (XRD), X-ray fluorescence spectrometry (XRF), glass sensors were applied. The glass and metal have been tested separately.

Keywords: induced corrosion, glass corrosion, metal corrosion, glass jewelry, glass sensor

INTRODUCTION

Glass is one of the oldest man-made substances ever produced. Its production began even before the beginning of human civilisation, being a natural product. So called **natural glass** is produced whenever glass-forming rocks melt under high temperatures and solidify quickly. This happens when volcanoes erupt (obsidian), when lightning strikes into quartziferous sand (fulgurites) or when meteorites hit the surface of the earth (tektites). Such naturally occurring glass, especially the volcanic glass obsidian, has been used by many Stone Age societies across the globe for the production of sharp cutting tools or weapons (arrowheads, spearheads, knives) and due to its limited sourcing areas, was extensively traded. Artificial glass, on the other hand, came only when civilizations began to form (Pfaender 1996, Lierke 2009).

Although it is not known precisely when glass was first made artificially by man, the oldest recovered artifacts (greenish glass beads) date back to 3500 BC. It is thought that glass-making originated in Egypt and Mesopotamia, but developed later and independently in China, Greece and

the Northern Tyrol. Ancient glass manufacture is believed to be linked to the production of ceramics or bronze, where it could have originated as a by-product.

The indigenous development of glass technology in South Asia may have begun in 1730 BC. Evidence of this culture includes a red-brown glass bead along with a hoard of beads dating to that period, making it the earliest attested glass from Indus Valley locations. Following ancient scripts written by Roman historian Pliny (AD 23–79), glass was discovered by Phoenician merchants transporting stone in the region of Syria almost 5000 BC. He says that merchants after landing, rested cooking pots on blocks of nitrate, with the intense heat of the fire placed on them. The blocks melted and mixed with the sand of the beach, forming an opaque liquid, accidentally. This story is more a reflection of Roman experience with glass production, nevertheless, the white silica sand from this area was used in the production of glass within the Roman Empire due to its low impurity levels.

The sophisticated technology needed to sustain glass manufacture derives from a variety of allied material technologies, predominantly ceramic and metal. There are needed to provide heat sources, tools, furnaces and material science, making its production really complex. All of those variables need to pre-date the use of glass within a society (Pfander 1996, Fuxi 2009).

In ancient times the most noteworthy limitation for glass fabrication was keeping the material chemically clean and homogeneous. This caused many technological problems and continuous modifications in the glass matrix. Furthermore, glass was a synthetic. This in itself was a sophisticated concept for a culture that was used to use materials that were already in existence: wood, bone, and stone or metal and clay (Lierke 2009). Glass in contrast, was the result of combining a mixture through heat. That is why all recipes of its fabrication have been kept in darkness for many centuries, and it is also why produced glass was seen to be a very desirable and prestigious product. Glass was seen as a material that could be made to imitate semi-precious stones, being accorded a status equal to that of the precious materials it imitated and thus, increased the social position of its owner.

Archeological evidence suggests that the first objects in which glass was used in their production were beads, plaques, inlays, and eventually small vessels. Glass jewellery such as rings, bead bracelets and necklaces became the most favourite decorations worn mostly by women but later, very often by men (Olczak & Jasiewiczowa 1963, Dekowna 1980). There was a wide array of techniques used by middle age artisans to give the glass its form, to connect it with other materials or even to give it a different colour, from using the inherent colour to form the impurity of glass materials or by adding colourants such as cooper or silver (Theophilus 1880).

During recent archeological excavations performed beneath the Market Square in Kraków, a large amount of rings were found, giving great knowledge into developed glass manufacture and putting some light on the international goods exchange and the life of the elite class in the medieval town (WAWEL 1000–2000). A few from this collection include a group of metallic rings mounting glass beads. The typology of the ring taken into account in this study is chronologically and geographically placed in Slavic Early Medieval Age, typically found in graves or settlements (Eggert 2010, Zabiegaj 2010, Greiner-Wronowa 2013). It is worth to note that glass rings were from a very small group of jewelry, quantitatively not recognizable across Slavic regions, while metal rings were and still are quite common if not universal across Europe (Sulimirski 1943, Stawiarska 1984). According to archaeological evidence, the largest accumulation of such rings was observed in Poland, especially in Kraków, which was one of the main European trade centers (Biezborodow 1956, Olczak 1959, Shelby 2005, Lierke 2009). That is why the presented samples have a very significant meaning. Moreover, the different origins of samples as well as the stratifications observed, found in different soil layers, improve the city environment changes for hundreds of years. In spite of that it can tell us how the local microclimate has affected the degradation of the analyzed rings, developing different corrosion processes.

In the case of research on glass and taking into account the historical character/value of the materials to be analyzed, it is absolutely necessary to employ only those methods of analysis which do not require addtional sample preparation. That is why close collaboration between technologists and conservators is necessary. To define the

glass-object stage, we have to cooperate with conservators in order to get more information about the previous storage and exposition conditions (Greiner-Wronowa 2005, Shelby 2005).

Nowadays, a wide spectrum of physical and chemical methods exist which help to determinate the corrosion products deposited on the material surface – even the chemical composition of the material from which the relics had been made. But a major problem is the amount and size of the original object used in research as in most cases, there is not enough to perform the necessary range of tests (Greiner-Wronowa 2005). Due to these limitations, a "glass sensor method" was developed and subsequently implemented. This method allows for the preparation of a **glass sensor** which replicates original historical objects with the same chemical composition and production attributes. The use of replicas of the original glass allows the user to perform an infinite number of tests without restriction (Greiner-Wronowa 2010).

The glass sensors samples were subjected to induced corrosion processes. The glass sensor used in this research was created based on the chemical composition of an eighteenth-century glass beaker. This sensor has the same chemical composition as an original antique glass with comparable chemical and physical properties, as well as similar reactive qualities. Selected corrosive agents (acid, water, etc.) were chosen on the basis of studies of the local environment of the glass-metal object. The corrosion processes induced on the glass

sensor took only a few weeks. The sensor can be subjected to a plethora of tests and the results reflect the processes occurring within the original place of storage. Stratifications that have arisen on the surface of glass sensors represent the corrosion products on real objects. It is important to diagnose the impact of the environment on the condition of original historical artifacts as deposits and corrosion layers on the surface of the material can be a catalyst for further deterioration.

MATERIALS AND METHODS

Due to the historical value of the ring the investigation was performed with limited micro invasive sampling to perform the investigation on a cross section by scanning electron microscopy. It was done according to the conservation agreement. Moreover, the reduced size of the objects allowed the direct investigation of them by Scanning Electron Microscopy connected with Energy Dispersive X-Ray Spectroscopy (SEM-EDXS). X-Ray Fluorescence spectroscopy (XRF) and X-Ray Diffraction (XRD) were additionally used to characterize the products causing alteration (Andrusieczko 1972, Kubiak & Gołaś red. 2005).

Considering that the chemical stability of glass depends on many parameters, it is worth to mention that the connection of two or more materials to build a single object provokes an increase in the system complexity that alters some important aspects such as chemical and mechanical durability.
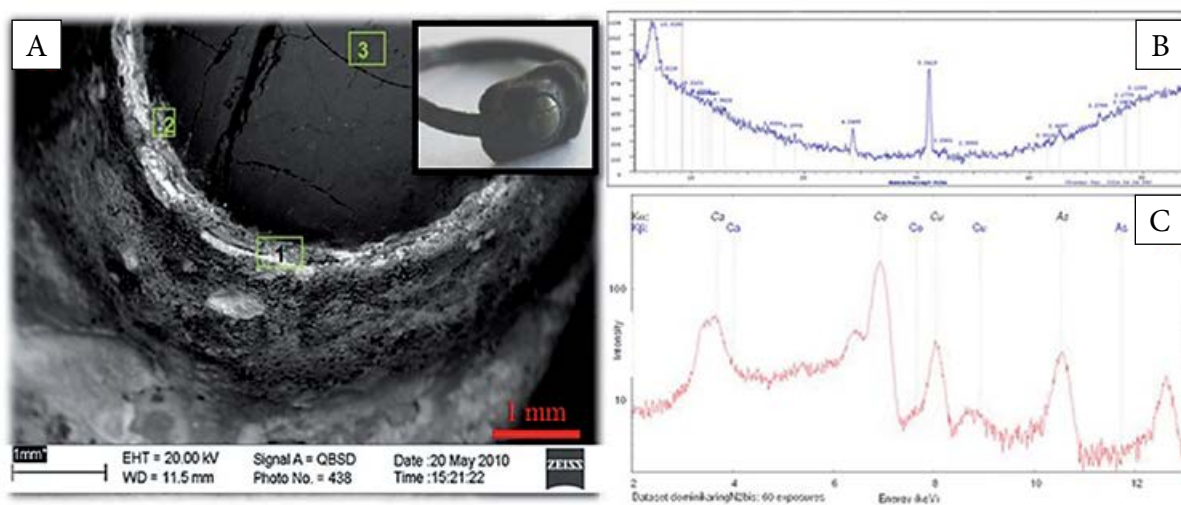

Fig. 1. *Analyses of the ring's crown: SEM micrograph of the glass bead and glass-metal joint pathology (A); XRD (B) and XRF (C) analyses of dispersed corrosion products from the glass-metal interface*

In addition to this, the mutual interaction between the different materials might be also affected by its reactivity, like in the presented ring. For this purpose, before to study on the alterations occurring at the glass-metal interface, it is necessary to consider each single material separately (Greiner-Wronowa 2013).

Analyses were carried out on three significant areas of the presented ring, for a glass pearl (Fig. 1A) and for a metal band: on the corroded band surface (Fig. 2A); on the altered layers of corrosion products of the metal band (Fig. 2B); and on the un-corroded alloy of the ring, after grinding (Fig. 2C).

The last important area where observations were focused on was the glass-metal connection. For this purpose, the white solid clay placed between the glass eye and ring's crown has been taken and dispersed for further analyses by XRD and XRF. A portable XRD apparatus (TERRA©) that works on powders, allows a fast collection of spectra in the angle range between 5° and 55° using CoKα wavelength. The excitement of powders generates a fluorescent signal that is collected for qualitative analyses (Fig. 1C). The latter confirmed the presence of Cu, As, and Ca while Co is due to the contribution of the X-ray source.

To improve the relevance of stratifications study of ancient subjects by induced corrosion, glass sensors were used to characterize the alteration products of the eighteenth century glass beaker (Greiner-Wronowa 2010). This sensor has the same chemical composition (Tab. 1) as an original antique glass with comparable chemical and physical properties, as well as similar reactive qualities. Glass with high alkali content ($Na_2O + K_2O$ = 15.22% wt.), with the addition of lead oxide is technically soft and called **technological long glass**. The prepared glass sensor was connected to the copper band and immersed in a 0.01 M solution of hydrogen chloride (HCl).

Table 1
The oxide composition of glass samples sensors [wt. %] of the eighteenth century ancient glass subject. The glass samples were connected to the metal and subjected to induced corrosion

Oxide composition	wt %	Oxide composition	wt %
SiO_2	73.94	Na_2O	0.84
CaO	9.26	BaO	0.14
K_2O	14.38	MgO	0.59
PbO	0.066	Al_2O_3	0.065
MnO	0.096	B_2O_3	0.64
Fe_2O_3	0.056	–	–

The reconstructed material was subjected to corrosion induced over a period of 20 weeks. To accelerate the corrosion of the sample, solutions were periodically subjected to an elevated temperature. Every other week, after 168 hours, they were placed in an elevated temperature of 40°C. Throughout the duration of inducing corrosion on the samples, macroscopic observations were made and changes in weight were registered. After observing the appearance of corrosion products and the structural changes of samples, detailed studies were carried out at the University of Genoa. SEM/EDS was performed with a scanning
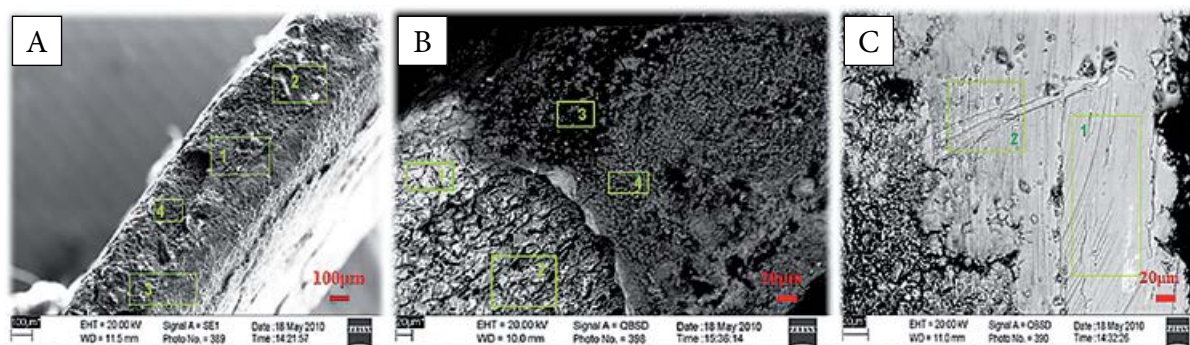

Fig. 2. *SEM micrographs of the metal parts of the ring: A) corroded metal band; B) alterated layers of corrosion products of the metal band; C) the uncorroded alloy of the ring, after grinding*

electron microscope, Carl Zeiss AG-EVO 40 Series and atomic emission spectroscopy – for identifying the solution (ICP-MS DRCII by Perkin-Elmer). In order to determine the phase composition of corrosion products, Raman spectroscopy was performed using a Leica Renishow DMLM spectrometer.

RESULTS AND DISCUSSION

The ring which is the subject of this study includes a metallic band and a blind glass bead (called "eye") mounted in a metallic "crown" (Fig. 1A). The entire surface of the ring as well as the cross sections are severely affected by corrosion. The corners and the edges show numerous deformations. In particular, the part where tiny metallic sheets are holding the glass bead in the crown, the corrosion produced several holes. Moreover, the glass itself has been damaged and shows many scratches. Especially on the most representative area of the bead where a deep elongated crater is visible. Because of stratifications on the glass surface it is almost impossible to define its original color. In order to investigate the external layers of corrosion, several areas of the surface were studied.

For the first set up of SEM observation, the metal part of the ring that was not in contact with the glass part was chosen (Fig. 2A). The obtained EDS data revealed copper and zinc as the main metallic elements (followed by a minor presence of tin and iron), characteristic of the corroded patina. Among the non-metallic elements sulfur and chlorine, together with oxygen, have the higher concentration.

An area where the corrosion caused some damage aided the observation of the metallic substrate (Fig. 2B) with its microstructural features. Crystals which are visible on the Figure 2B are well shaped and polygonal. Going up from the lower parts of the corroded stratifications, it is possible to see a few different layers of corrosion products. Chemical analyses show that the oxidized layer which is in direct contact with metal is richer in zinc but covered by the homogeneous layer of copper sulphide. An amount of phosphor has also been detected.

Furthermore, the chemical nature of the alloy has been confirmed by the compositional analysis of the uncovered metallic substrate, showing EDS spectra typical for brass with a low amount of tin.

Copper, zinc and tin are coming from the metallic substrate while iron, calcium, sulphur, phosphor and chlorine are obviously a contamination due to its deposition in soil. In order to quantitatively analyze and confirm this information, it was necessary to eliminate the patina and directly analyze the metal. An area where corrosive metallic substrates were slightly grinded is shown in Figure 2C. An EDXS standard analyses in areas 1 and 2 of Figure 2C confirmed the nature of the brass alloy with copper (82% at.), zinc (17% at.) and only 1% at. of tin. No lead was found in this sample.

The examination of the surface around the glass eye under the microscope revealed the presence of numerous flaking and pitting phenomena. Corrosive blooms and stratifications make the glass strongly corroded. The network of cracks covers the entire sample and the central part of the bead is heavily damaged by a deep fracture.

Chemical analyses show two dominated elements, copper and calcium. What is worth mentioning is that copper is present on the edge of the "eye" but not on the top of the bead. In contrast, calcium is measured all over the surface of the glass. High concentrations of these chemical elements are a consequence of glass corrosion (Fig. 1). In the more corroded areas, leaching (long contact with water) and the redistribution of soluble components (mainly alkaline) leads to the partial dissolution of the silicate network and the formation of micro-craters in the surface (Vilariques et al. 2010). Furthermore, the silica gel on the "eye" surface is enriched with iron, sulfur and phosphor. Those have been stratified on the glass due to reactions with the surrounding environment (e.g. soil) (Greiner-Wronowa et al. 2007).

Moreover, the surface of the glass is also covered by inorganic material with a noticeable presence of arsenic and calcium, especially close to the borders where the junction with the metal part is situated. For this reason a small amount of this material was sampled to undergo a characterization by powder XRD (Fig. 1B) and a qualitative XRF analyses (Fig. 1B).

The analyses confirmed that the white deposit consisted of calcium and arsenic oxides mixed with a copper compound. Due the limited amount of powder, special equipment was used. XRF and XRD examinations of white corrosion products, as the one shown in the SEM micrograph in

Figure 1A, spread all over the glass surface, showing enrichments in Ca and Arsenic. The calcium found is consistent with a glass corrosion mechanism, but arsenic does not come from the glass matrix or from the metal alloy, that the metal band is built of. It is well known that Pb can be used as a filler of broken or missing parts in Cu based objects (Gimeno 2008), acting as glue between the brass sheet and the brittle glass bead during the manufacture of the ring. Moreover, the lead can present a certain amount of arsenic as dopant. However, the experimental evidence shows the presence of arsenic but lead was not found in the samples. A possible explanation for this apparent inconsistent result can be attributed to the environmental degradation (for hundreds of years) than can provoke the dissolution of the Pb, leading to a concentration of arsenic in the sample (Jokubonis 2003). It is anyway interesting to note

how a deep insight into such historical objects can open perspectives of research and discussion.

The sample representing the combination of a glass element with copper was subjected to a battery of tests. The application of an acidic solution represented the aggressive environment and initiated the reaction of chlorides on the metal and glass (Fig. 3A). The copper band was dissolved in 0.1 M HCl, and the resulting reaction formed a green crystalline corrosion on the entire surface of the glass and metal (Fig. 3B). Furthermore, the acid solution discolored and the reaction of the chloride ion with copper resulted in the precipitation of the product being crystallized over the entire surface of glass sensor. Weight loss suggests the presence of a dissolving phenomenon of the metal components in harsh environments, indicating broad changes in the glass-metal objects during degradation.
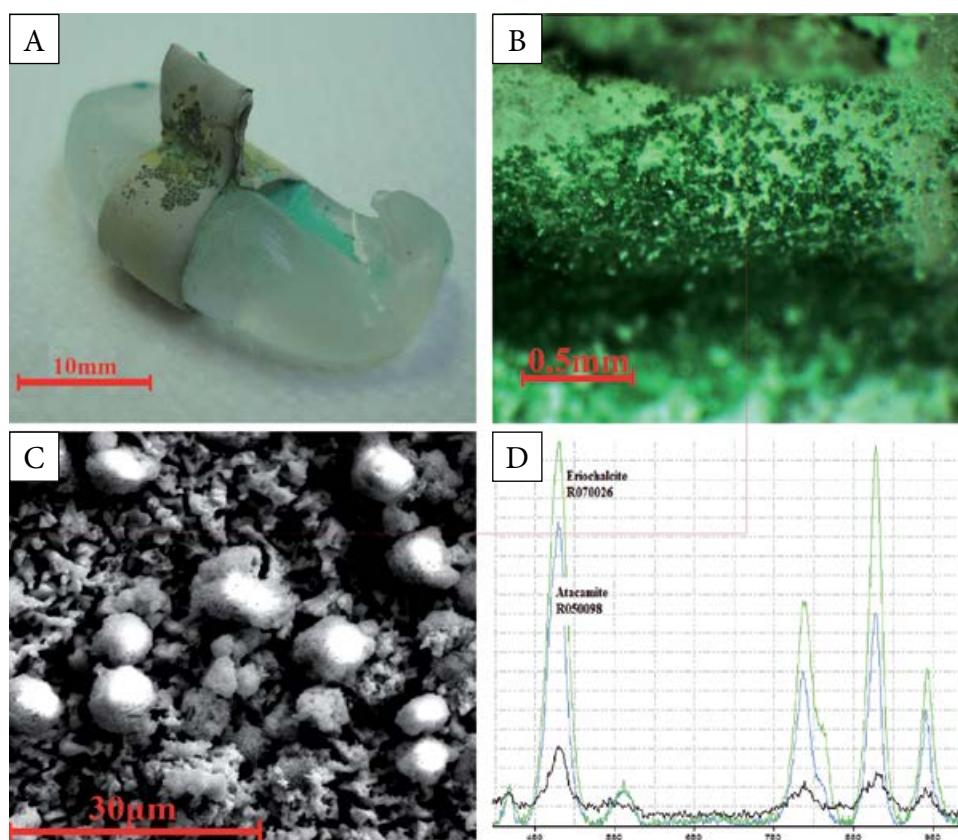

Fig. 3. *Analysis of the glass sensor: A) observation after 2 weeks, sample immersed in 0.01 M HCl; B) pictures of the samples after 20 weeks of induced corrosion of the samples in aqueous solutions, Wild Leica M8 stereoscope; C) the morphology of the surface, SEM/EDS analysis of the sample; D) Raman spectroscopy, Leica Renishow DMLM spectrometer. Line legend: black – experimental sample, blue and green – spectra of individual minerals (from RRUFF™ Project). Numbers R050098 and R070026 are RRUFF ID (database of Raman spectra, X-ray diffraction and chemistry data for minerals)*

To examine the surface morphology and initially diagnose the chemical composition of the surface stratification, a SEM/ES analysis was performed. For the sample, thirteen measurements in total were made. Most of the analysis showed that the corrosion product is a compound of copper (Cu), oxygen (O) and chlorine (Cl) (Fig. 3C). Also noted was the presence of carbon (C), at a concentration of less than 7% by weight. It is very difficult to describe the shape of the crystallites. RS was analyzed to determine the phase composition.

For sample D, only one measurement by Raman spectroscopy (Leica Renishow DMLM) was performed on the green powder, because the corrosion product was on the whole surface of the sample and the solution. This apparatus uses two lasers at 514 nm and 785 nm. A single beam spectrometer was used, with a camera connected to the confocal microscope and the imaging filter set to dispersive Raman imaging. The products have been identified as atacamite – $Cu_2Cl(OH)_3$ and eriochalcite – $CuCl_2 \cdot 2H_2O$ (Fig. 3D). The first one belongs to the group of halides. It is perfectly pointed; the crystals are green, have a diamond shine and crystallized in a rhombic pattern. This mineral occurs in clusters, is needle-like and is clearly visible under the scanning electron microscope. This was shown to be an Eriochalcite crystallized ortho-rhombic system, a rare mineral which has a greenish-blue color.

The corrosive solutions of 0.01 M HCl were examined after some time of induced corrosion, using atomic emission spectroscopy with Inductively Coupled Plasma to diagnose the presence of metals and some non-metal elements. Attention was paid to the high concentration of calcium (47.1 mg/L). It can therefore be claimed that the alkaline cations in the glass structure are exchanged with chloride ions from the solution. This is confirmed by the measurable concentration of sodium and potassium. Structure-building elements of glass are detected in the solution at high concentrations (K = 8.0 mg/L and Na = 8.4 mg/L). This demonstrates the glass-metal corrosion in acidic solutions. Metal ties are also dissolved at low pH levels which exhibits very high concentrations of copper (Cu = 6400 mg/L).

Previous studies were limited by the number of samples. The presented method allows the elucidation of the mechanism of corrosion of historical objects through the use of the so-called "Glass sensors" method. It is a great complement to traditional testing methods of historical objects.

CONCLUSIONS

This paper contributes to the investigations into the history, technology and degradation of middle age objects recently excavated under the Main Square in Kraków (Poland). The historical sample presented here belongs to a narrow group of metallic rings with mounted glass beads which were discovered in different ground layers in Kraków. All of the applied analyses were concentrated on the different corrosion stratifications which covered all parts of the ring, strongly damaging the glass bead as well as the metallic band and crown. The glass eye was mostly covered with silica gel and more advanced corrosion has been found nearby metallic sheets connected with glass bead, while the metal band was degraded by the corrosion processes completely. To recognize the chemical composition of the surface deposits, the glass and metal investigations were carried out separately.

Moreover, the study of medieval glass pearl rings allows quantification of the glass and metal alteration under natural conditions over periods of time of up to millennium. The analyses show that glass alteration is not only due to surface reactions caused by water penetration. Therefore, its degradation can be affected by differentiating surroundings (micro-climate) such as humidity, soil contamination, industry development or environment changes which, in fact, provoke different corrosion processes locally. Also, it is worth noting that the high level of jewelry manufacture (Olczak & Jasiewiczowa 1963, Dekowna 1980, Eggert 2010) of the rings contribute to the knowledge of local history giving insights over the development of colonization in Krakow corresponding to the upper classes of the population dealing with the exchange of goods with foreign countries (WAWEL 1000–2000, Fuxi 2009).

Research conducted on the glass sensor can be considered as a real model for corrosion phenomena expansion, in this case, in an acidic environment (having in mind a acidic pH of the soil). Macroscopic and microscopic observations provided information about the corrosion's direction and the intensity of the processes. In an environment of hydrochloric acid (0.01 M HCl) applied

to the glass sensor sample, it is clear that the band made of copper is not resistant and undergoes a process of dissolving, forming deposits on the surface of the glass, metal, and between these materials. Corrosion tends to start from the weakest materials and the formed corrosion products could induce the next stage of deterioration. The parameters for storing glass objects connected by two (or more) materials must be very well matched in order to avoid corrosion developing on one or two components. Usually the weakest began the deterioration process. Research shows that glass does not like to be kept in or near moisture and that metal is mostly sensitive to chlorides. Extensive tests allowed for the identification of the characteristics of the formed stratification.

The presented studies are a great evidence of why close collaboration between technologists and conservators is a necessity as possible to determinate a definitive condition of a historical object and apply the best methodology to ensure its conservation. Most importantly, materials such as these with historical value need to be protected in order to provide future generations with evidence of civilizations past.

REFERENCES

Andrusieczko A., 1972. *Technologia szkła: praca zbiorowa.* Arkady, Warszawa.

Biezborodow M.A., 1956. Driewnierusskije stiekła i ognieupornyje izdielija. *Kratkije Soobszczenija IIMK*, 62, 79.

Dekówna M., 1980. *Szkło w Europie wczesnośredniowiecznej.* Zakład Narodowy im. Ossolińskich, Wrocław.

Eggert G., 2010. Corroding glass, corroding metals: survey of joint metal-glass corrosion products on historic objects. *Corrosion Engineering, Science and Technology*, 45, 5, 414–419.

Fuxi G., Brill R.H. & Shouyun T., 2009. *Ancient Glass Research along the Silk Road.* World Scientific Publishing Company.

Gimeno D., Garcia-Valles M., Fernandez-Turiel J.L., Bazzocchi F., Aulinas M., Puges M., Tarozzi C., Riccardi M.P., Basso E., Fortina C., Mendera M. & Messiga B., 2008. From Siena to Barcelona: Deciphering colour recipes of Na-rich Mediterranean stained glass windows at the XII–XIV century transition. *Journal of Cultural Heritage*, 9, 10–15.

Greiner-Wronowa E., 2005. Metoda sensorów szklanych w analizie przemian chemicznych korozji szkła. *Świat Szkła*, 5, 64–67.

Greiner-Wronowa E., 2010. Sensory szklane-metoda wczesnego monitorowania mikroklimatu w muzeum. *Szkło i Ceramika*, 3, 12–17.

Greiner-Wronowa E., Pusoska A. & Piasecka J., 2007. Biały nalot na obiektach szklanych w gablotach muzealnych. *Szkło i Ceramika*, 1, 26–31.

Greiner-Wronowa E., Zabiegaj D. & Piccardo P., 2013. Glass-metal objects from archaeological excavation: corrosion study. *Applied Physics A*, 113, 999–1008.

Jokubonis C., Wobrauschek P., Zamini S., Karwowski M., Trnka G. & Stadler P., 2003. Results of quantitative analysis of Celtic glass artefacts by energy dispersive X-ray fluorescence spectroscopy. *Spectrochimica Acta Part B*, 58, 627–633.

Kubiak WW. & Gołaś J. (red.), 2005. *Instrumentalne metody analizy chemicznej.* Wydawnictwo Naukowe „Akapit", Kraków.

Lierke R., 2009. *Die nicht-geblasenen antiken Glasgefässe: ihre Herstellung von den Anfängen bis zu den Luxusgläsern der Römer.* Deutsche Glastechnische Gesellschaft.

Olczak J., 1959. Proizwodstwo stieklanych pierstniej na slowanskoj territorii w srednije wieka. *Sowietskaja Archeologija*, 3, 81–83.

Olczak J., Jasiewiczowa E., 1963. *Szklarstwo wczesnośredniowiecznego Wolina.* Muzeum Pomorza Zachodniego, Szczecin.

Pfaender H.G., 1996. *Schott Guide to Glass.* 2nd ed. Chapman & Hall, London.

Shelby J.E., 2005. *Introduction to Glass Science and Technology.* 2nd ed. The Royal Society of Chemistry, London.

Stawiarska T., 1984. *Szkła z okresu wpływów rzymskich z północnej Polski. Studium technologiczne.* Zakład Narodowy im. Ossolińskich, Wrocław.

Sulimirski T., 1943. Faience beads in the Polish Bronze Age. *Man*, 139, 124–125.

Theophilus, 1880. *Teofila kapłana i zakonnika o sztukach rozmaitych ksiąg troje* [księga 2: *O pierścieniach*]. Akademia Umiejętności, Kraków.

Vilarigues M., Redol P., Machado A., Rodrigues P.A., Alves L.C. & Silva R.C., 2010. Corrosion of 15th and early 16th century stained glass from monastery of Batalha studied with external ion beam. *Materials Characterization*, 22, 40–52.

WAWEL 1000–2000, *Biuletyn Informacyjny Biura Prasowego Kraków 2000*, 32, 2000, [on-line:] http://www.krakow2000.pl/biuletyn/biuletyn_32.html.

Zabiegaj D., 2010. *Zmiany korozyjne biżuterii szklanej z prac archeologicznych pod Rynkiem Głównym w Krakowie.* AGH, Kraków [M.Sc. thesis].

True and fake red layers
on the objects from archaeological and historical context: microscopic observations

Joanna Trąbska[1], Barbara Trybalska[2]

[1]*Rzeszów University, Institute of Archaeology; ul. Moniuszki 10, 35-015 Rzeszów;
e-mail: joanna.trabska@archeologia.rzeszow.pl*
[2]*AGH University of Science and Technology, Department of Material Engineering and Ceramics;
al. Mickiewicza 30, 30-059 Krakow, Poland; e-mail: barbara.trybalska@wp.pl*

Abstract: Colored layers on surfaces of objects associated with archaeological and historical context may be of various origins: natural or intentional and in numerous cases their exact identification is not obvious, especially for thousand-year-old objects. Yet, the diagnosing of their nature may constitute an important element for the interpretation of ancient cultures. Examples of red color layers of natural, intentional and unclear origin were chosen and observed to select criteria defining layers of uncertain parentage.

Keywords: archaeology, red layers, paintings, weathering crusts

INTRODUCTION

Colored layers on surfaces of objects associated with archaeological and historical context may have been produced by humans deliberately or "made" by nature; they may have arisen in a natural way, but have been generated by the specific cultural context. Colorful layer may appear because of restorers' interventions: introduction of a colored layer consciously or because of product time discoloration. In extreme cases, one must reckon with counterfeiting. In any situation, it is important to identify a substance which formed the layer and to determine how it contacts with the ground, how thick and how homogeneous it is; perhaps also to detect a specific painting technique or traces of tools employed in a painting process. It is crucial to define the natural and cultural context from which the item originates.

Red was the first true color attractive to humans (Petru 2006), and evidences of interest in it reach deep into Paleolithic. In a distant time span, it is particularly difficult to distinguish between intentional and the natural colors or the imposition of one to another. Diagnosing of their nature may constitute an important element for the interpretation of the dawn of human culture.

The problem of discrimination between intentional and natural red layer refers to not only paintings but also fine-grained or cryptocrystalline iron-bearing crusty concentrations of other origin. They may be remnants of rubbing red powders into various supports (Behrmann & Gonzales 2009 – Fig. 5), even very specific, like a cemented, phosphatized ash from a hearth dated to 58,000 BP (Sibudu, South Africa, Wadley 2010). Red crusts appear on skeletal surfaces due to unknown actions: rubbing a powder into a body, rubbing it into

a skeleton, applying a suspension, spraying a red dust or others. Cracks and crevices may have been infilled with red remnants after exploitation of a red raw material; it is a case of the Lovas site (Hungary & Dobosi 2006). Many sculptures and reliefs, now discolored, are believed to have been painted but only microscopic traces may support these hypotheses (Roussot 1994, Behrmann & Gonzales 2009).

Archaeological artifacts may have become casually contaminated by red powder dispersed in a sediment due to intentional actions (such concentrations are known from numerous sites, e.g. the Fumane cave, Broglio et al. 2007), due to their immersion in red ash layers (present e.g. at the Dolni Věstonice I and Milovice sites, Moravia & Oliva 2007) or natural red regolith of terra rosa type, abundant in numerous southern European caves (e.g. Odile & Plassard 1995). Nevertheless, to the authors' knowledge, no hard evidence of such contamination has been proved so far.

Paintings and irregular patches that happen to occur together (e.g. the Aurignacian paintings from the Fumane cave, Broglio et al. 2007) can be discerned when the two are compared on the basis of microstratigraphy and petrographic analyses. In many dubious cases, an intentional action of painting may be identified due to specific appearance of a smoothened underground, infilling and evening of microundulation (e.g. Trąbska 2001); however, for many rock, cave, shell or stone paintings it does not occur (e.g. Broglio et al. 2007: 167).

Usually, thickness of paintings executed with mineral pigments balances close to 0.2 mm (e.g. Roy 1993, Berry 2007). The pigments used to be very fine-grained and of homogeneous size, due to careful grinding (the phenomenon observed also for the rock paintings, e.g. Hoz de Vicente, Hernanz et al. 2010) but their particular appearance will always depend on an individual workshop or painting technique. However, micromorphological features of a pigment itself may appear indicative especially because ground iron-bearing pigments tend to preserve their parental microstructure (Trąbska et al., manuscript). In this way, the particles micromorphology may indicate an external source of a raw material, different from *in situ* source. In some cases, hematite ordering may indicate at a pigment origin (Trąbska & Gaweł 2007, Hernanz et al. 2010). Unfortunately, detailed comparative analyses may be misleading.

Microstructure and chemical composition of a potential intentional layer may perfectly reflect the analogous features of a widespread red rocks from the surroundings. Some red paintings from the Fumane Cave were executed with a pigment of a composition identical with the pigment of the cave's terra rosa (Broglio et al. 2007).

To numerous paintings, even as ancient as Paleolithic, specific extenders used to be added (Martin 1993: 261–264, Behrmann & Gonzales 2009). They tend to be different from an underground and the recipes are repeatable, so that their presence points at human executed panting. Analyses of organic bindings are not so promising, especially for very old crusts and paintings (e.g. Paleolithic), excluding waxes, stable within very long periods of time (Riparo Dalmeri Cave, Rosanò & Pelizzaro 2005).

Iron compounds often precipitate on bone or shell surfaces producing brown-red and red coloration. It may appear difficult to discern results of painting, rubbing, immersing or other human actions. Influence of natural processes is suggested by domination of brownish shade (especially in a moderate climate), irregularity of patches contour, only partial covering of an object. The objects that have been interpreted as intentionally colored are usually red or cherry on a whole surface and a color shade is uniform (compare, for example, Aurignacian ivory pendants from the Betche-aux-Rotches cave, Lejeune 2007: 143). It should be remembered that some restoration processes may have altered original appearance.

Intentional layers that are most difficult to discern from natural crusts come from Paleolithic, mainly due to time span and simpler or unknown way of their execution compared to numerous younger realizations. Microscopic cross-sections of cave, rock, shell or stone paintings depict various images: panting layers are cryptocrystalline or fine-grained, usually the layers are clearly discernible from an underneath but the contact may be both sharp (especially for cryptocrystalline paint, e.g. Hoz de Vicente, Hernanz et al. 2010) or cloudy (for fine-grained paint; Fumane Cave, Broglio et al. 2007: 167; Abri Pataud, Chiotti et al. 2007). Painting layers may be inserted between layers of clay minerals, gypsum, oxalates and other secondary phases (e.g. Hoz de Vicente rock art, Hernanz et al. 2010).

Last but not least, red colored surfaces were influenced by deterioration: continuity of the layers got lost (e.g. some paintings from the Yiwarlarlay in Australian North Territory, Watchman et al. 2000), images disappeared due to powdering (e.g. Behrmann and Gonzales point at the phenomenon for certain paintings from the Siega Verde cave, 2009). Coloration was likely present on reliefs from Cap Blanc (Roussot 1994) but its nature may be interpreted only based on the analyses of microtrace remnants. A change of phase composition of red iron pigments is less possible than for other pigments but in some circumstances it is still possible.

In this paper, selected examples of red color layers of natural, intentional and unclear origin are presented. They were identified on the objects and surfaces: (a) from an archaeological context/historical context, (b) from natural environment, (c) obtained in experimental research. Basic information on tested material is listed in the Table 1. Observation and characteristics of the well-defined color origin layers and layers of natural origin will enhance an extraction of criteria defining layers of uncertain parentage.

Samples were observed under polarized light microscope Olympus BX 51. Further tests were carried out on the scanning microscope NanoNova FEI Company, with an ISIS Link Oxford microanalyser. Samples were covered with graphite. A low vacuum technique was applied. Samples were observed in 3D dimensions, sometimes on surfaces of thin sections.

RESEARCH

Historical context unspecified. Intentional red layers

A case: Mural paintings (Vrbnik, Croatia). Red paint layer can be implemented using a wide range of pigments, dyes and adhesives (Berrie 2007). A sample comes from a depiction of a foundation cross from ruined stone chapel. Painting layers were executed with an inorganic pigment.

Thickness of a painting layer is uneven but oscillates around 0.2 mm. It penetrates into a very fine-grained carbonate underneath. The contact is apparent but not very sharp, as if the painting was realized on a soft underlayer. Painting layer is composed of cryptocrystalline microclusters of iron compounds and fine grains of detritic quartz, feldspars and glauconite (Fig. 1). Small red remains of the painting layer are still recognizable due to features of microstructure. Layer surface is far from being perfectly smoothened (Fig. 2) but it may have been deteriorated. Features of the red painting reflect the features of terra rosa abundant in the nearby area (Trąbska et al., Data Base of Red Ferruginous Raw Materials, manuscript).

Table 1
The origin of the layers and objects, and applied research methods

| Context	Subject	Site	Research methods
Historical context undetermined, red layer is intentional	Mural painting of unknown age	Vrbnik, Krk, Croatia	PLM
Natural layer	Weathering crusts	Annaberg, Beveaux, Kasina Wlk., Strążyski Stream (The Tatra Mountains), Jawor-Bolków, Jaroszowiec, Brno	PLM
Experimental red layer	A bone immersed in a cherry suspension of an iron-bearing claystone	Authors' research, also Trąbska (2009)	PLM, SEM/EDS
Archaeological context defined, red layer of dubious origin	A skull surface covered with a red layer	Upper Paleolithic site Brno II (Moravia, Czech)	PLM, SEM/EDS
	Surface of a stony pavement from a grave	Neolithic site Książnice (Poland)	PLM, SEM/EDS
	Surface of a bone covered with a red layer	The Przeworsk Culture site, Gać (Poland)	PLM
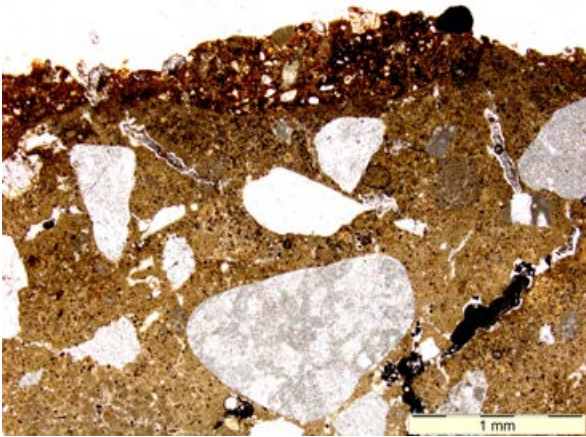
Fig. 1. *Mural painting, Vrbnik, Croatia. Red layer of an uneven thickness, cracky and grainy, penetrating into the substrate. PLM, one polarizer*
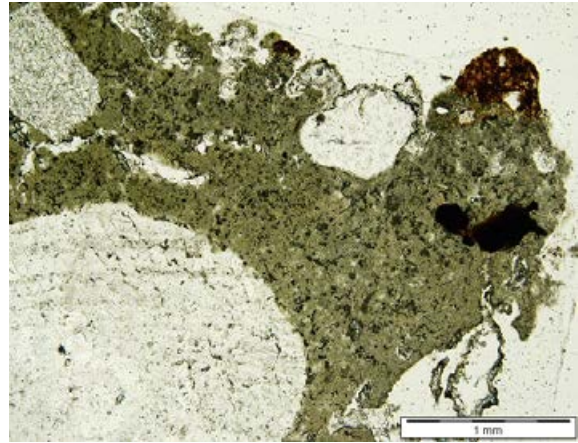

Fig. 2. *A remnant of a mural painting from Vrbnik, still recognizable as part of the painting layer. PLM, one polarizer*
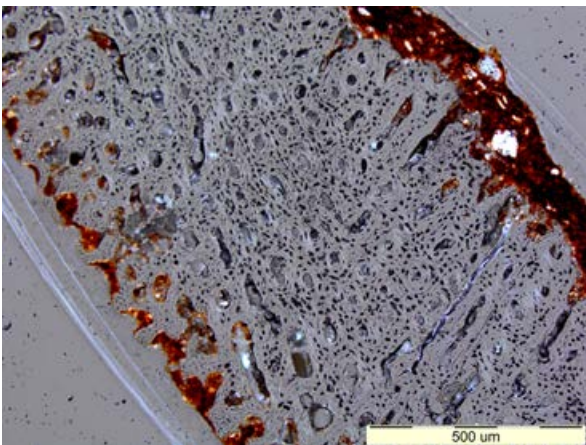

Fig. 3. *A cross-section of a colored bone. The inner part on the right side of the photograph. Polarizer partially crossed*
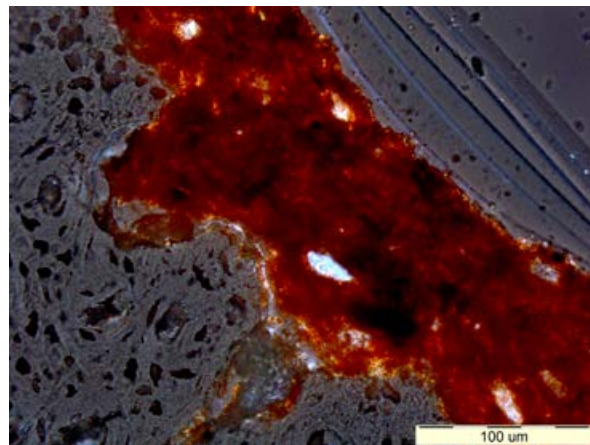

Fig. 4. *A fragment of a red layer with visible compact mineral sheets. Polarizers partially crossed*
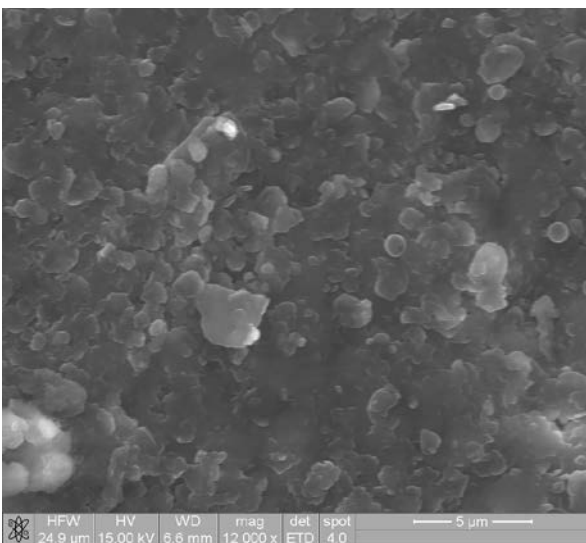
Fig. 5. *A fragment of a red layer with erythrocytes and sheets of clay minerals. Magnification 12,000×*
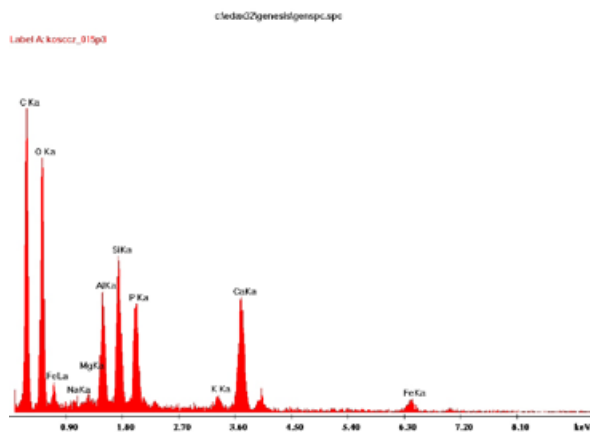
Fig. 6. *EDS spectrum of the red layer. Strong apatite signal is worth noting*

Context: the experiment

The experiment involved immersing of a bone in a suspension manufactured from a mixture of Lower Triassic cherry claystone and water. Thin-walled bone, of whitened and bleached surface belonged to a small animal and was found in the field. The bone was immersed for a few minutes.

Both surfaces of the bones and large number of pores and channels have been covered or filled with red suspension (Fig. 3). The layer is homogeneous, consists of sheet minerals, cryptocrystalline iron-compound lumps and detritic components of the parental rock (Figs 3, 4). Parallel clay sheets arrangement remains recognizable. The surface of red layer is smooth, but not perfectly. The thickness does not exceed 0.2 mm. Similar characteristics were observed in the case of shells submerged in the same suspension (Trąbska 2009).

SEM/EDS analysis reveals predominantly flaky clay minerals and single erythrocytes; the latter may be explained by young, "non-archaeological" age of the bone (Fig. 5). The chemical composition of the sample revealed bone calcium and phosphorus; the other elements reflect a chemical composition of the Baranów clays (Fig. 6) (Trąbska et al. Data Base of Red Ferruginous Raw Materials, manuscript).

Context: natural "layers" of weathering crusts

In consequence of weathering processes, thin red crusts form on various rocks surfaces. Some of these layers may illusionary resemble layers of painting or other intentionally executed layers (Figs 7–10, esp. Figs 9, 10, 13); examples of their variability are presented on the photographs.

Annaberg (Erzgebirge, Germany). Sample was collected in the village of Annaberg, Erzgebirge, in an artificial outcrop. A granitoide boulder, approximately with a diameter of 3 cm, was completely covered with a red crust of cryptocrystalline iron compounds. In the PLM image it appears to be a quite thick (about 1 mm), almost opaque layer with scarce irregular voids, filled with iron compounds. Cryptocrystalline iron oxyferroxides penetrate into the surface of the granitoide and provoke scaling off the most external rock parts, as well as fill into the natural cracks (Fig. 7).
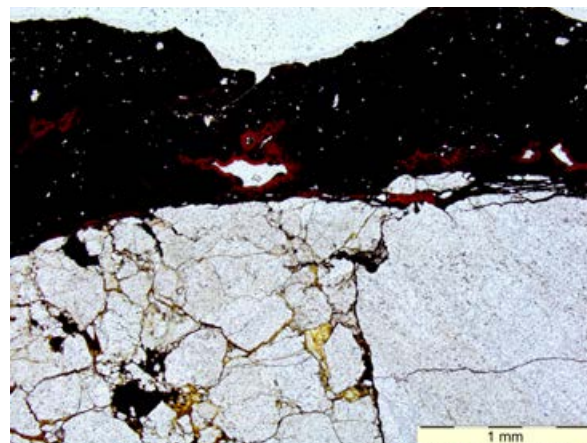

Fig. 7. Annaberg. PLM, one polarizer

Beveaux (Switzerland). On the surface on the pelitic-aleuritic iron rich rock, derived from the morainic area of the Neuchatel Lake shore, a dark red coat of a constant thickness of approximately 0.5 mm was formed. Microscopically, red shade is unevenly distributed, with the lower part of the layer darker than the upper. Structurally the layer is very similar to the ground and contacts with it rather sharply (Fig. 8).
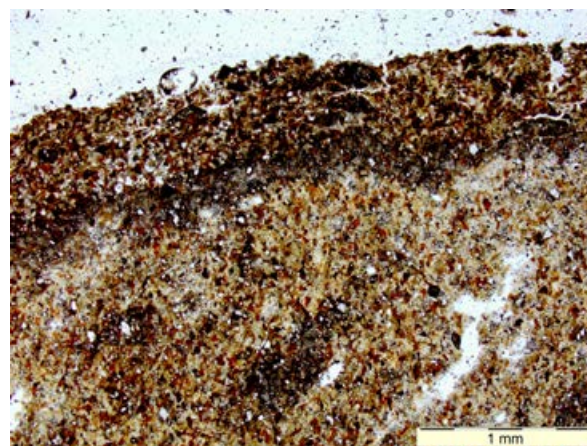

Fig. 8. Beveaux. PLM, one polarizer

Kasina Wielka (Poland). The sample comes from a clayey weathering crust on variegated slate of the Magura Unit. A dark red layer formed on the surface of the red rocks. Red layer, characterized by a more or less constant thickness of about 0.2 mm, fine-grained structure and discontinuity, separates sharply from the underneath of the parental rock. The layer is homogeneous in terms of the composition.
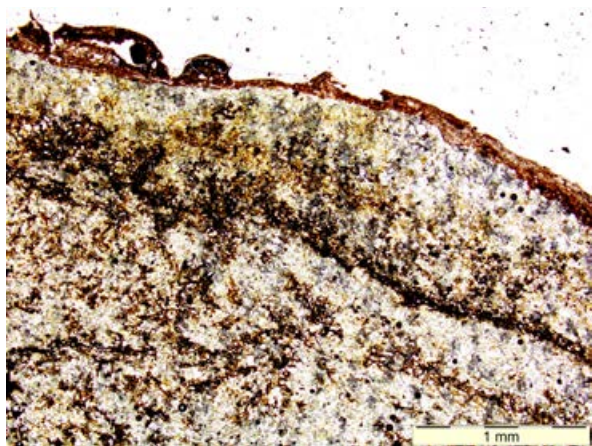
Fig. 9. *Kasina Wielka. PLM, one polarizer*

High concentration of iron compounds, compared to the parental rock might suggest the resemblance to painting layers (Fig. 9).

The Tatra Mountains – Strążyska (Poland). The sample is a pebble from the Strążyski Stream. The surface of the sample is almost completely covered with cherry coating of cryptocrystalline iron compounds. The rock was deformed by sedimentary or metamorphic processes. Iron compounds are accumulated in the rock in the form of irregular streaks. Weathering processes resulted in the migration and accumulation of iron compounds on the surface of the pebble. The covering layer filled pebble's irregularities. Contact of the layer with the ground is very sharp and it penetrates deep into the surface of the pebble and into microcracks. In consequence, the components of the primary rock are immersed in the red crust.

It is worth noting that the surface is very well-smoothened by natural processes. Layer thickness is uneven, up to 0.2 mm (Fig. 10).

Jawor-Bolków (Poland). The sample comes from clayey weathering crust formed on the eruptive rocks of the Rotliegend.

Fig. 11. *Jawor-Bolków. Explanations in the text. PLM, one polarizer*

The most external surface layer is a red-colored soil originated on volcanic rocks substrate. Red layer as a whole is characterized by diverse thickness. Phase composition also varies: detritic grains are submerged in cryptocrystalline iron unions. Contact with the parental rock is sharp. Patchy concentrations of iron compounds form opaque stripes within the volcanic glass. On the surface, they form a very thin layer under the soil dirt. This cover is discontinuous, very thin, and has a sharp contact with the ground (Fig. 11).
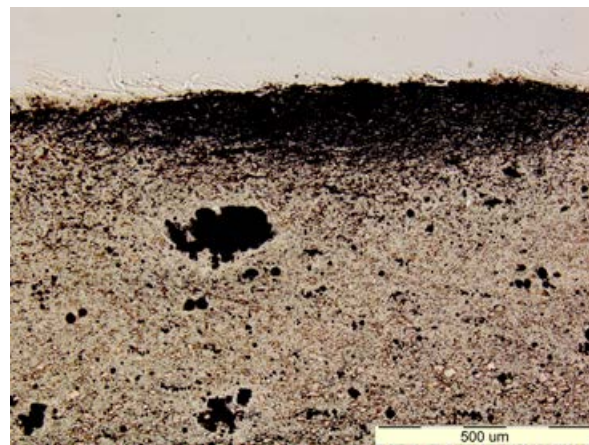

Fig. 10. *The Tatra Mountains – Strążyski Stream. PLM, one polarizer*

Fig. 12. *Jaroszowiec. Explanations in the text. PLM, one polarizer*

Jaroszowiec (Poland). The sample represents a cherry micritic dolomite. In the rock volume, opaque rectangular phases are distributed; the thick, lenticular and uneven cherry crust formed on the rock surface is also composed of the same phases. The contact with the ground is blurred (Fig. 12). The most probably, the opaque grains are pyrite, weathered to hematite during warm and/or dry geological periods.

Brno (Moravia, Czech Republic). The sample represents a trachyandesitic or trachybasaltic pebble from Devonian conglomerate with a cherry surface, homogeneous, 0.2 mm thick. Surface layer is quite smooth. Contact with the rock substrate is sharp but uneven. The layer is homogeneous in terms of the composition, with occasional plagioclases (Figs 13, 14).
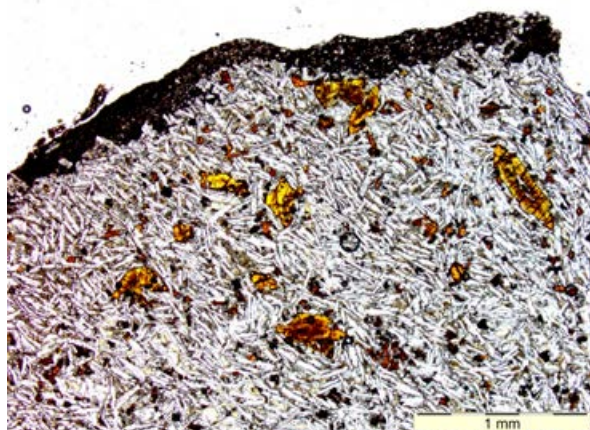

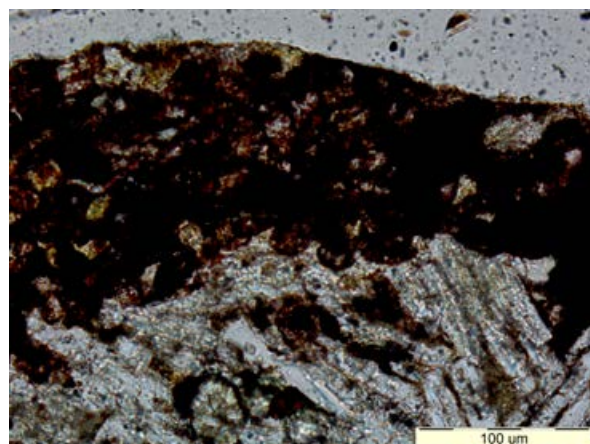***Fig. 13.*** *Brno. Explanations in the text. PLM, one polarizer – sample 1*

Fig. 14. *Brno (a detail). Explanations in the text. PLM, one polarizer – sample 2*

Context well defined, the origin of the layers unclear

A case: a red layer on the surface of the skull, Brno II site. The Upper Paleolithic Brno II site was discovered in the late 19th century in one of the districts of Brno and re-explored in the second half of the 20th century. It was located on the sands and gravels of the Svitava River floodplains, covered with loess, close to various crystalline and carbonates rocks. Bones of mammoth, rhinoceros and humans, and stones were found there. Human bones were colored red. The sample skull belonged to a man known as a shaman; the skull surface was covered with a number of notches (Oliva 1996).

Small fragments of the skull bones were collected in the Anthropos Museum in Brno. The bone is gray, covered one-side by a thin red layer. The layer does not flake off, adheres well to the ground (Fig. 15). The surface of the skull under the red layer is different from the surface of a modern man skull as well as Neolithic humans (Simel'nikov 1963, Tab. 48; 51n). In addition, this surface is not smooth and is barb (Figs 15, 16).

Fig. 15. *A fragment of the skull surface with a red layer that fills the uneven ground. PLM, one polarizer*

Colorful layer adheres to this surface filling microscopic inequalities (Figs 15, 16). The layer is not continuous and of a variable thickness, but not exceeding 0.5 mm; it is grainy but homogeneous as far as the mineral composition is concerned. Irregular concentrations of oxides and/or iron hydroxides, angular clumps of calcium carbonate and clay minerals in lumps and rock matrix were detected (Fig. 16). In terms of chemical
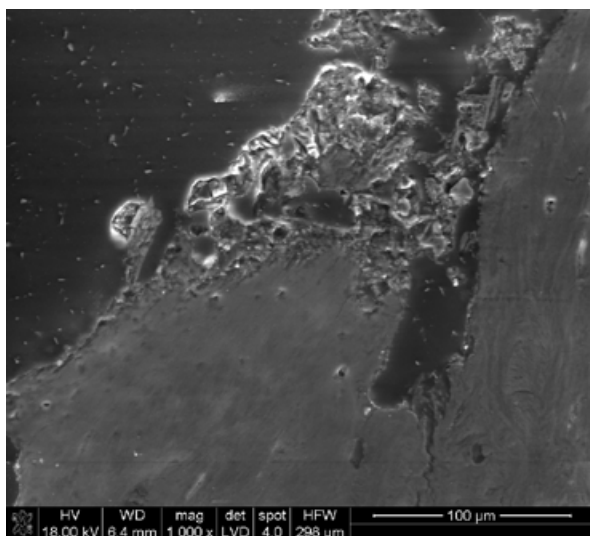
Fig. 16. *Unevenness of the skull surface. An arrow points at calcium phosphate (bone, most probably) grain. Magnification 1000×*

composition magnesium and potassium alumosilicates as well as iron phases are present (Figs 17, 18). A small amount of phosphorus in a form of dispersed, very cryptocrystalline (Fig. 17) phase(s) as well as single angular lumps, situated close to the surface of the skull (Fig. 16) were observed everywhere within the red layer.

A case: red crust on a stony pavement. A pavement (Fig. 19) was a part of the Neolithic Złockie Culture's grave, located at the Książnice site (Poland). The site occupied Quarternary loess of the Pińczów Hills, with a watercourse located about 300 m westwards. The tombs were constructed as burial niches and the near-niche pits. Skeletons and grave goods (pottery and objects made of stone and horn are located at a depth of 125–145 cm (Wilk et al. 2011).
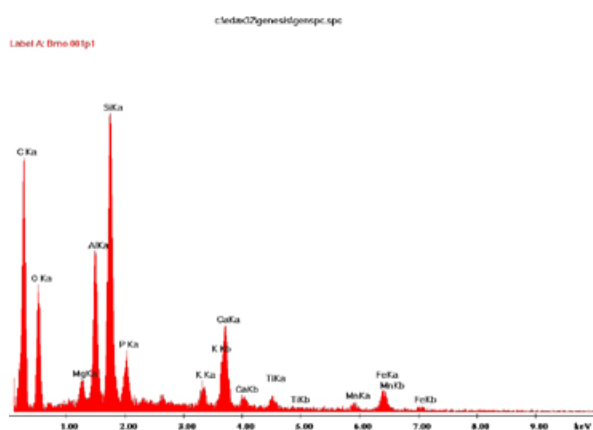

Fig. 17. *EDS spectrum. Composition of clayey areas of the red layer*
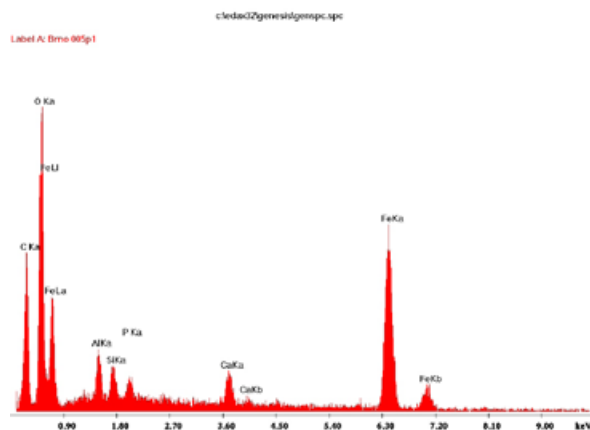

Fig. 18. *EDS spectrum. Composition of iron compounds concentration within the red layer. Note a high concentration of alumina, compared to silica*

Fig. 19. *Grave pavement covered with a red coating*

Fig. 20. *One of the stones of the pavement*

The bottom of the niche is covered with white stone; the artifacts were distributed over its surface. The surface of the stone is red-orange, continuous or cracked (Fig. 20).

At the site, migration phenomena of iron compounds are common and result in yellow-orange streaks on the profiles' walls and compact crusts on the loose pebbles. Pavement stones include opokas and spikulites (Figs 19, 20).

An explanation of the red film nature on the pavement surface was especially important due to the context of sacred space and a fact of transporting the stone from a distance of ca. 20 km (Walczowski 1978).

Red and orange layers are characterized by a uniform thickness not exceeding 0.5 mm, very good adherence to the ground and a "cloudy", soft contact with it (Figs 19, 20, 22, 23). They are entirely cryptocrystalline; its surface is smooth (Figs 19, 21) or uneven (Figs 20, 22). Within the visible layers, there are tiny fragments of the underlying rock (Figs 21, 23). The bedrock was discolored (Fig. 19) on the thickness of about 0.5 mm.
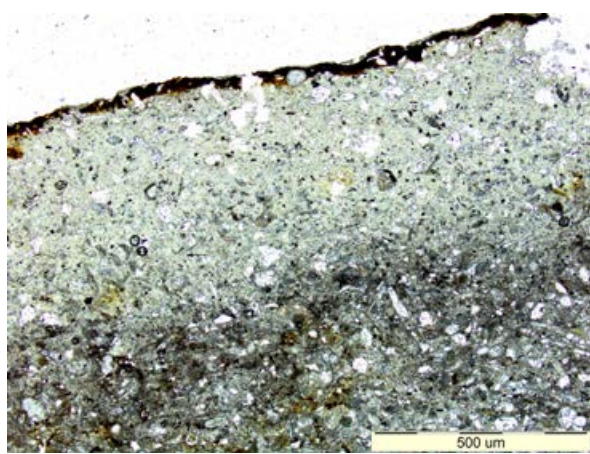

Fig. 21. Red layer on the surface of the calcitic opoka. PLM, one polarizer

PLM and SEM image reveals fine-grained and homogeneous appearance of the layer surface (Figs 23, 24). Its morphological diversity is revealed under a greater magnification: corroded authigenic quartz crystals (Fig. 25, p. 1) and oval agglomerates of silica are present. There are also concentrations of silica enriched in aluminum, magnesium, potassium and iron (Fig. 25, p. 3). Everywhere the amount of iron is very low (Figs 26, 27).
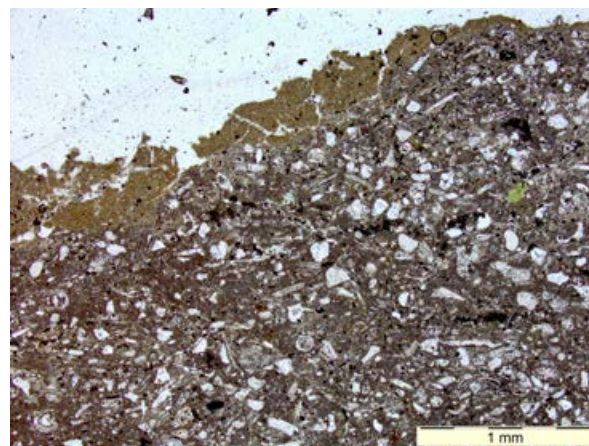

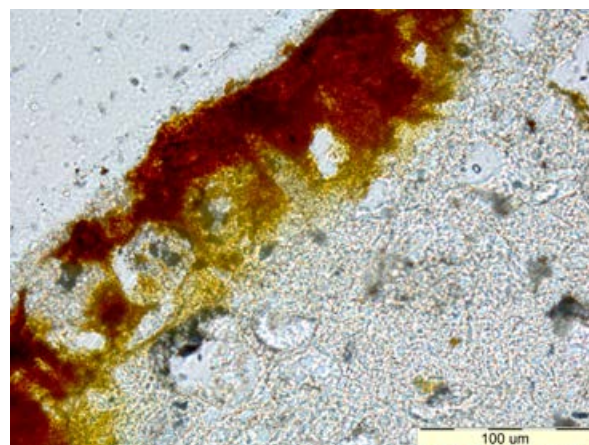*Fig. 22.* Yellow-brown, cryptocrystalline crust on the opoka surface. PLM, one polarizer

Fig. 23. Red crust with grains of primary rock. The crust is uniformly cryptocrystalline. PLM, one polarizer

A case: red layer on the surface of the bone. A bone fragment originates from the site Gać near Przeworsk (Subcarpathia, Poland), representing the Przeworsk Culture. It was found in the cremation gravesite, which was located on clay; it was an arable land at the time of the first exploration. Burial is situated on "a vast clayey plateau with slopes falling toward the low-lying meadows". Burnt bones were placed in urns and put into pits dug in the yellow clay, surrounded and covered with ashes, dusty burnt clay, shells and twisted iron weapon (Hadaczek 1909).

The bone was found in a grave, besides equipped with 5 iron items (*inter alia*, umbo and scissors), tentatively dated to *phase B2* of the *Roman Period* (Anna Lasota, unpublished). The bone fragment is covered with a red layer, macroscopically uniform, well adhering to the substrate.
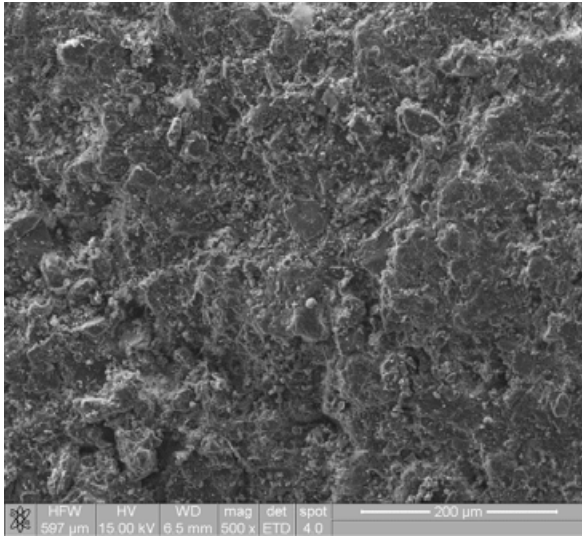
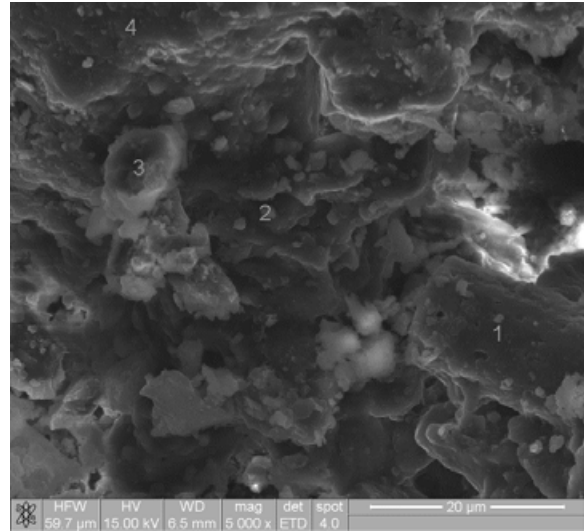**Fig. 24.** *Homogeneous and fine-grained red surface layer. Magnification 500×*

Fig. 25. *The red surface composed mainly of silica and a small amount of iron. Magnification 1500×*
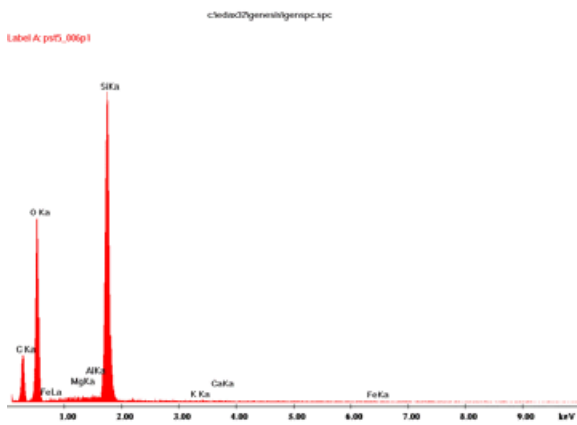

Fig. 26. *EDS spectrum. Chemical composition of the surface in points 1 and 3*
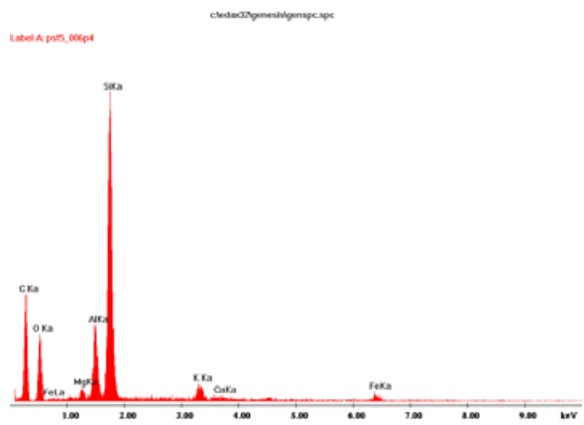

Fig. 27. *EDS spectrum. Chemical composition of the surface in points 2 and 4*
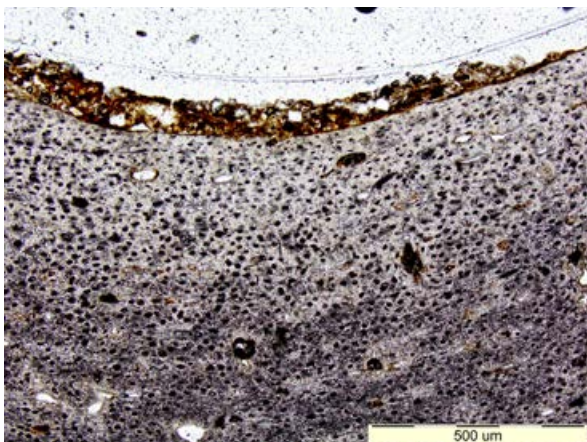

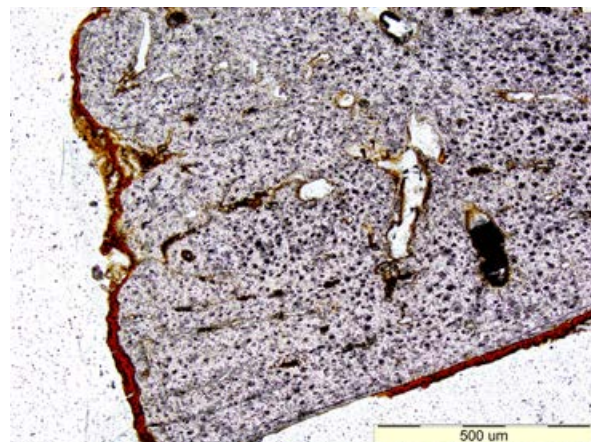**Fig. 28.** *Heterogeneity of the layer A. PLM, one polarizer*

Fig. 29. *Layer B: present on all surfaces of the bone. PLM, one polarizer*
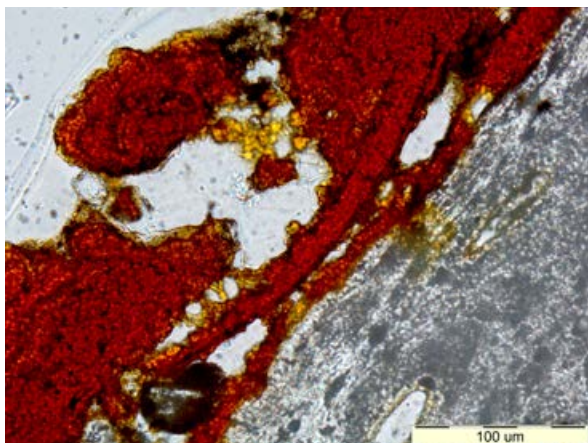
Fig. 30. *Layer B. Collomorphic and crusty appearance of the layer. The bacterial (?) threads close to the bone surface. PLM, one polarizer*
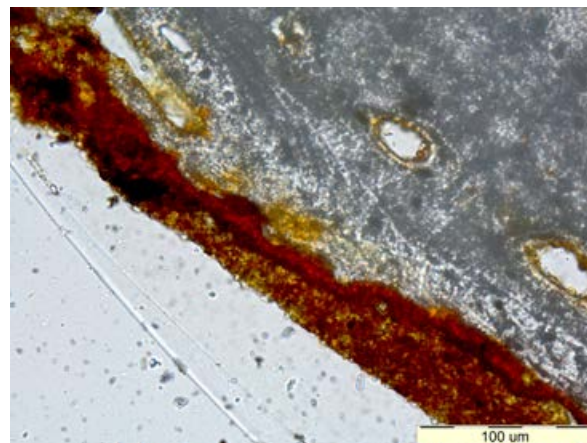
Fig. 31. *Layer B. Bipartite layer. PLM, one polarizer*

The crust is located on the external and internal parts. Red layer has three appearances; therefore, it will be further described as layer A, B and C.

Layer A is characterized by thickness not exceeding 0.2 µm; it sticks well to the smooth bone underneath; it is homogeneous in terms of composition and phase but multiphased (Fig. 28). Pores and channels are filled with an opaque substance (ash?) and iron compounds. The layer A is present only on the inner side of the bone.

Layer B reveals a diverse thickness; it is cryptocrystalline and homogeneous. It covers both internal and external surfaces of the bone (Fig. 29). It is characterized by flaky, crusty and collomorphic constitution with threads of bacterial or fungi origin (Fig. 30). The layer is bipartite (Fig. 31).

Layer C is characterized by a homogeneous, cryptocrystalline, fine granular morphology, the thickness of about 0.1 mm, cracks perpendicular to the substrate, sometimes the presence of granular substances within a layer or between the layers of a bone.

Discussion of dubious cases (the Brno II, Książnice and Gać sites)

Identification of the origin of a red layer on the surface of the skull from the Upper Paleolithic Brno II site is compelling due to the fact of deliberate damage of the skull surface and the likely redeposition of the remains of the deceased (Oliva 1996). The layer morphology indicates that presumably a raw, non-processed, material was used: a natural mixture of fine-grained detritic quartz,

clay minerals and cryptocrystalline compounds of iron. Small lumps of calcium carbonate may indicate a genetic relationship with a carbonate rock, although the contamination from the surrounding loess cannot be ruled out (although, in fact, its chemical composition is unknown to us). High concentration of aluminum suggests the influence of alite weathering of a raw material, which is why the *occurrence of* terra rosa is probable.

Presence of grains of calcium phosphate in the red layer may indicate the rubbing of paint into the surface of the skull. However, accidental scaling off a bone fragment from the damaged skull surface cannot be ruled out.

A hypothesis about the natural origin of the red layer may be supported by its morphological similarity to natural dirt (Fig. 11). However, such red agglomerates (natural or burnt) have not been evidenced in the site's vicinity (Oliva 1996); additionally, only an external skull surface is reddened. Micromorphology of the red layer resembles the micromorphology of the painting from Vrbnik (Figs 1, 2) or the experimental immersion (Figs 3, 4). No traces of an action of painting could have been proven but other modes of color application were possible (rubbing a roughly prepared red powder into the skull surface or application of a thick suspension).

Due to the intentional transport of stone slabs and their careful organization on the grave floor at the Książnice site it may seem that the red layer on a stony pavement should have been painted purposely. Environmental and morphological

reasons suggest, however, that this is a layer of natural origin. The environment, in which the grave is located, is loess, where iron compounds have been migrating. Calcitic opoka, relatively easily soluble in weakly acidic environment, changes pH on the slab surfaces into neutral or alkaline. These conditions contribute to dissolving and reprecipitation of silica (documented on the Figure 25), adsorptive for iron compounds. Debris of opoka from underneath was immersed in uniformly cryptocrystalline red and orange crust; it is characteristic for the crust of natural origin.

Nevertheless, without detailed observations, nature of the layer may have been misinterpreted. Characteristics of the red layers on a bone from the Gać site, labeled as A, B, C, indicate that they are of natural origin. It might be confirmed by a cover on all the surfaces of the bone and especially by the collomorphic, uniform nature of iron compounds of layers B and C. In turn, layer A, with inhomogeneous structure, fills the bone from the inside. The substance within layer A and partially layer C is similar to the mineral soil or/and ash contamination. Therefore, it seems probable that a layer of iron oxides and/or hydroxides closes the mineral dirt and likely some post-cremation contaminants. Variety of morphology of red layers suggests their formation at different times. Dried up layer C seems to be older than layer B; it is hard to determine the age of layer A. Iron compounds may have originated either from the surrounding rocks or corroded iron objects, unless the latter were covered with fire patina (sealed with a layer of hematite).

DISCUSSION AND SUMMARY

Painting layers of any age, when a mineral pigment is used, are characterized by, more or less, a thickness of 0.2 mm and a detectable, usually sharp contact with the ground. Paints can penetrate into the substrate when they are too thin or ground is too wet. Painting layers, especially younger than Paleolithic, were usually executed on a prepared underneath. If grains of pigments can be detected under a high-magnification PLM, they reveal a uniform size and shape. Usually, there are no impurities associated with raw materials or their amount is low but intentional extenders may have

been present. Organic adhesives can often be evidenced in historical paintings (e.g. Roy 1993, Berrie 2007); their identification is more complex in archaeological painting and other layers. When carefully processed, the separate components of paint may be detected, only with difficulty, under PLM; scanning microscope is more effective. Painting layers may be deteriorated, subsequently their continuity is usually lost but even then they may be identified (Fig. 2).

If red layers were not a result of a painting action but spraying a red powder on a surface, rubbing it in dry into it, or applying a suspension, some above-mentioned features may disappear; especially a careful paint preparation, among others grinding pigments or addition of extender according to determined recipes.

Colorful layer obtained in the experiment is characterized by a uniform thickness not exceeding 0.2 mm. The layer penetrates into the ground, fills pores of bones and smoothens unevennesses. Although levigation process was applied, clay minerals and detritic quartz grains are still detectable, indicating the type of raw material (Figs 3, 4). They differ from natural crusts (Fig. 28) in their multiphase structure, lack of organogenic remains and lack of deep penetration into a bone pores. In most cases, the natural layers are cryptocrystalline.

Natural layers on rocks are of diverse thickness, different structural similarity to the substrate (extreme examples include Annaberg and Beveaux; Figs 9, 10), various contact with the ground. In most cases, the crusts are composed of cryptocrystalline iron compounds, frequently with incorporated fragments of underlying, parental rocks. Sometimes (sample Jawor-Bolków) natural crust overlaps with a layer of dirt from the environment, in this case also red. Sometimes red crusts are delusively similar to intentionally executed crusts (compare Figs 11 and 15).

Therefore, several criteria, that allow to discern natural and intentional red layers in dubious cases, in accordance with the premise of the work, can be proposed (Tab. 2).

FINAL CONCLUSIONS

The cryptocrystallinity and continuity are mostly (but not always) the features that apparently indicate a natural origin of red layers.

Table 2
Specific features of intentional and natural red layers

Example	Specific features
Paintings on a prepared underneath	Layers are narrow, of a uniform thickness, close to 0.2 mm. Painting layer is usually structurally homogeneous. Contact with the ground is usually sharp. Cloudy penetration of a red layer into an underground is possible. Specific extenders may be present. Textural (parallel, wavy) indicators of a painting process may be detectable. Possible fillings of cracks of an underground by a red layer are possible. An underground is usually intentionally prepared. Pigments in PLM image are very small or invisible. Pigments micromorphology, hematite ordering and chemical composition may (but not necessarily) differ from the analogous features of natural weathering crusts from the surroundings
Paintings on a rough underneath	As above, but: an underground may be unprepared (usually cave, rock and stone paintings), a painting layer may be wavy, discontinuous (as above)
Intentional layers other than paintings	Does not need to be continuous. May be multiphased. Red component does not need to have been prepared (e.g. ground). May be of various thickness, but still not exceeding significantly 0.2 mm. Underlayer is not intentionally prepared considering a painting action (e.g. smoothened). A contact between a layer and underneath may be very irregular. Specific features of an underneath or specific admixtures may be indicative
Experimental layer	Homogeneous and compact layer. Penetrates into the porous substrate (due to quite thin suspension). Raw material features possible to decipher. Layer thickness comparable with painting layers
Natural crusts	Homogeneous crust often structurally resembles an underneath. Contact with the ground varies (is "cloudy" or very sharp). Remnants of a parental rock may be included into crusts. Thickness may be identical as for painting layers. Compactness may be identical as for painting layers. Very irregular thickness is possible. Scaling off is possible. Collomorphic appearance is very common

Based on the discerned criteria (Tab. 2) we have classified a red layer on a surface of a bone from the Gać site and the Książnice site as natural, a red layer on a shaman skull from the Brno II site as intentional. In all cases, we have also analyzed environmental factors promoting a mobility of iron compounds as well as geological setting. Composition of red layers may indicate a determined raw material, or, at least, material that does not occur in the object's vicinity. Criteria of thickness and a variety of a contact with the ground as well as smoothness of a surface are not decisive: many natural layers are confusingly similar to intentional layers. The possibility of overlapping of several crusts or painting layers and crusts cannot be neglected. We have observed the phenomenon for a "natural" sample (sample Jawor-Bolków) and a sample originated from a site (Gać); the latter recognized also as a natural. It should be remembered that colored layers of any origin may bear information on surroundings.

REFERENCES

Behrmann R. & Gonzales J., 2009. Les colorants de l'art paléolithique dans les grottes et en plein air. *L'Anthropologie*, 113, 559–601.

Berrie B. (ed.), 2007. *Artists' Pigments. A Handbook of Their History and Characteristics. Vol. 4*. Washington – London.

Broglio A., Giachi G., Gurioli F. & Pallecchi P., 2007. Les peintures aurignaciennes de la grotte de Fumane. [in:] Floss H. & Rouquerol N. (eds), *Les chemins de l'art aurignacien en Europe. Editions Musée-forum Aurignac*, Cahier 4, 157–170.

Chiotti L., Delluc B. & Delluc G., 2007. Art et parure aurigneciens de l'Abri Pataud (Les Eyzies-de-Tayac, Dordogne, France) dans le contexte aurignacien du Perigord. [in:] Floss H. & Rouquerol N. (eds), *Les chemins de l'art aurignacien en Europe. Editions Mesée-forum Aurignac*, Cahier 4, 171–185.

Dobosi V.T., 2006. Lovas (Hungary) ochre mine reconsidered. [in:] Körlin G. & Weisgerber G. (eds), *Stone Age – Mining Age. VIII Internationales Feuerstein Symposium im Deutschen Bergbau Museum Bochum 1999. Veröffentlichungen aus dem Deutchen Bergbau Museum Bochum 148/Der Anschnitt Beih*, 19 (Bochum 2006), 29–36.

Hadaczek K., 1909. *Cmentarzysko ciałopalne koło Przeworska* [series: *Teka Konserwatorska*, 3, 2]. Grono C.K. Konserwatorów Galicyi Wschodniej, Lwów.

Hernanz A., Ruiz-Lopez J.F., Gavira-Vallejo J.M., Martin S. & Gavrilenko E., 2010. Raman microscopy of prehistoric rock paintings from the Hoz de Vicente, Minglanilla, Cuenca, Spain. *Journal of Raman Spectroscopy*, 41, 1394–1399.

Lejeune M., 2007. Le Trou Magrite et l'art mobilier aurignacien en Belgique: synthese et problemes. [in:] Floss H. & Rouquerol N. (eds), *Les chemins de l'art aurignacien en Europe. Editions Mesée-forum Aurignac*, Cahier 4, 131–144.

Martin Y., 1993. Analyse des pigments. [in:] *L'art Pariétal Paléolithique. Techniques et méthodes d'étude*, Paris 1993, 261–264.

Odile M. & Plassard J., 1995. *Visiting Rouffignac Cave*. Bordeaux.

Oliva M., 1996. Mladopaleolitycky hrob Brno II jako príspěvek k počátkum šamanismu. *Archeologické rozhledy*, 48, 3, 353–383.

Oliva M., 2007. *Gravettien na Moravě*. Praha – Brno.

Petru S., 2006. Red, black or white? The dawn of colour symbolism. *Documenta Praehistorica*, 33, 1–6.

Rosanò P. & Pelizzaro S. 2005. Analisi chimico-stratigrafico di tre pietre dipinte con ocra. [in:] Broglio A. & Dalmeri G. (eds), *Pitture paleolitiche nelle Prealpi Venete. Grotta di Fumane e Riparo Dalmeri*, Cierre Edizioni, Verona, 139–143.

Roussot A., 1994. *Visiter le Cap Blanc*. Bordeaux.

Roy A. (ed.), 1993. *Artists' Pigments. A Handbook of Their History and Characteristics. Vol. 2*. Washington – London.

Simelʹnikov R.D., 1963. *Atlas anatomii čeloveka. Tom 1: Učenie o kostâh, soedinenie kostej i myšcah*. Gosudarstvennoe izdatelʹstvo medicinskoj literatury, Moskva – Leningrad.

Trąbska J. 2001. *Mineralogical and chemical study of painting layers of Medieval wall paintings from Poland* [series: *Prace Mineralogiczne*, 90]. Polska Akademia Nauk, Kraków.

Trąbska J., 2009. Microstructure of haematite powder: an udervalued indicator in interpretation of ferruginous raw material manufacuring, using and provenance. *Śląskie Sprawozdania Archeologiczne*, 51, 5–13.

Trąbska J. & Gaweł A., 2007. Microstructural features of powdered haematite as a promising factor in provenance studies. *Sprawozdania Archeologiczne*, 59, 41–48.

Trąbska J., Trybalska B. & Gaweł A. [in preparation]. Data Base of Red Ferruginous Raw Materials.

Walczowski A., 1978. *Szczegółowa mapa geologiczna Polski w skali 1:50 000, arkusz Bejsce (949)*. Warszawa.

Wilk S., Haduch E., Szczepanek A., Koszowska E. & Trąbska J., 2011. Groby z nadpalonymi szkieletami z cmentarzyska kultury złockiej w Książnicach, woj. świętokrzyskie. [in:] Jaszewska A. & Michalak A. (red.), *Ogień – żywioł ujarzmiony i nieujarzmiony. VI Polsko-Niemieckie Spotkania Archeologiczne, Garbicz, 5–6 czerwca 2008 r.*, Stowarzyszenie Naukowe Archeologów Polskich. Oddział Lubuski, Zielona Góra, 23–54.

http://www.geology.cz/app/ciselniky/lokalizace/show_map.php?mapa=g50zj&y=597467&x=1160307&r=7500&s=1&legselect=0.